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(58) Field of Search

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C7F FAHE FAHL FAHM FAHP FAHX FARE FARL
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INT CL⁵ B21B, B23P, B24C, C23C
ONLINE DATABASES: WPI, CLAIMS

(54) Treating MCrAlZ layers by material-moving machining and then heat treating

(57) After a MCrAlZ layer is applied to a thermally stressed engine component, wherein M is a metal and Z is an active element from the group of the rare earths, yttrium, hafnium, silicon or scandium, on thermally stressed engine components, a material-removing machining is first performed for smoothing and setting the thickness of the layer and then a heat treatment of the smoothed coating is performed. Coatings may thus be obtained which have a high degree of enrichment of active elements on the surface of the layer and a high degree of resistance to thermocyclic stressing. The MCrAlZ may be applied by a low-pressure plasma injection method or by a PVD method. A heat-insulating layer of CaO, MgO, Y₂O₃, Yb₂O₃, CeO₂ or HfO₂ may also be applied.

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FIG. 1

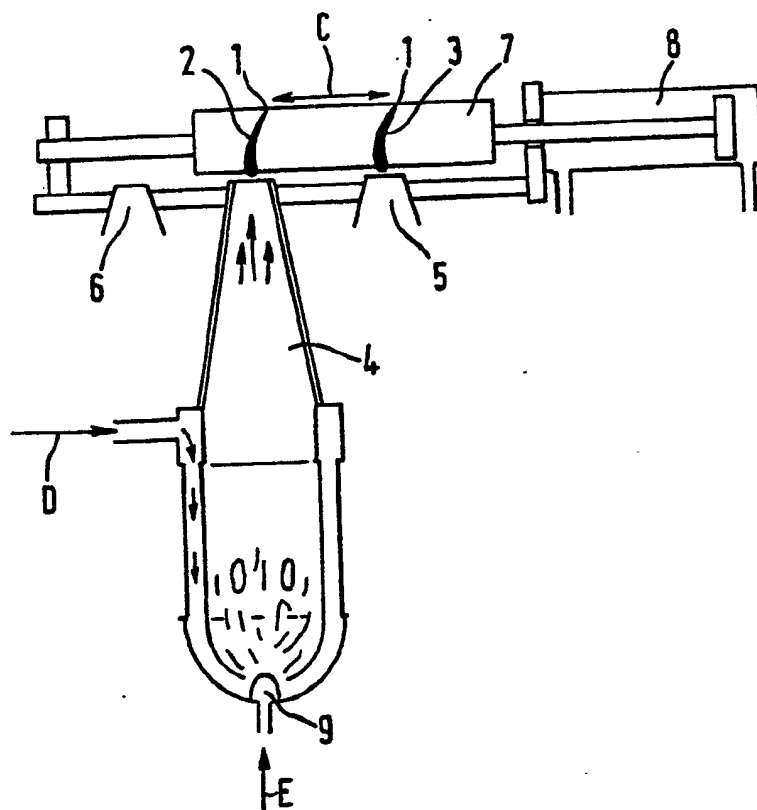


FIG. 2

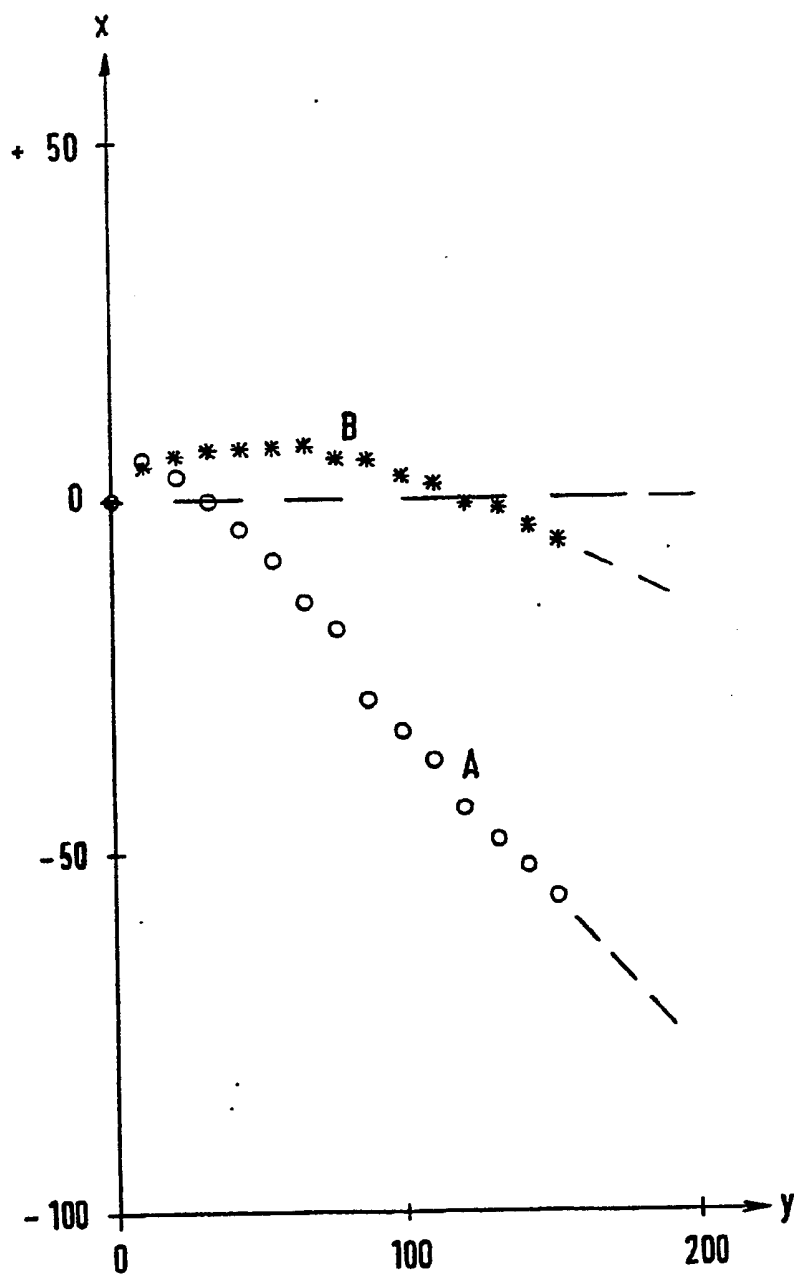


FIG. 3

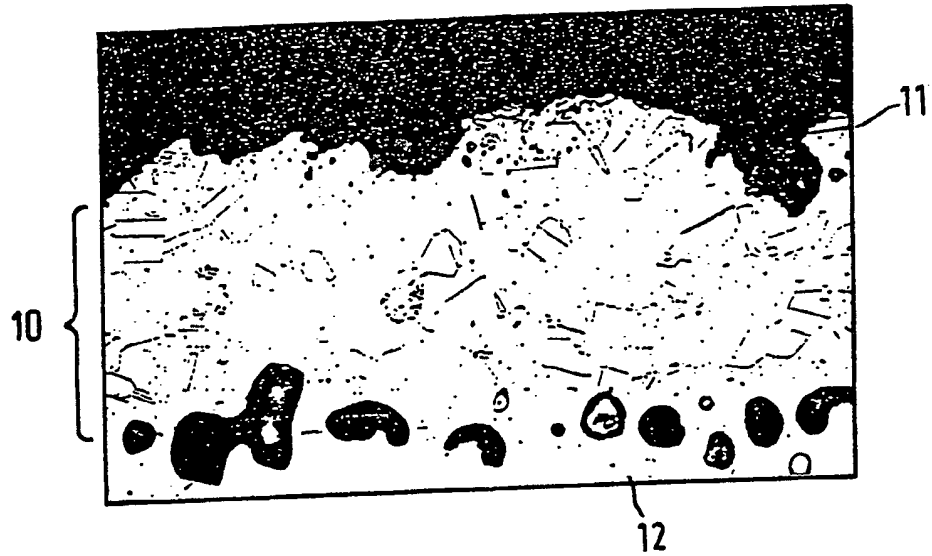


FIG. 4

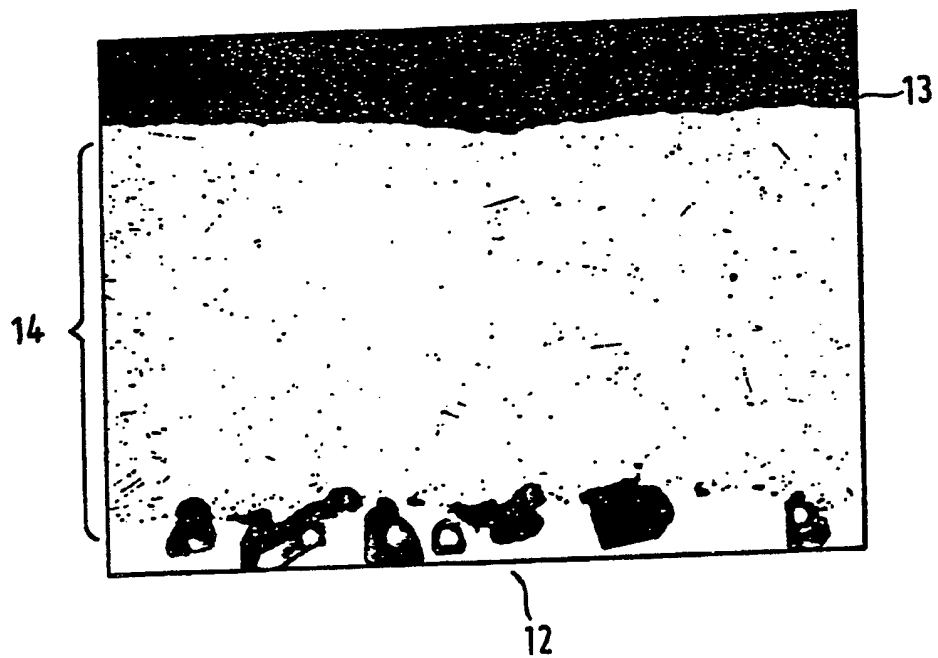
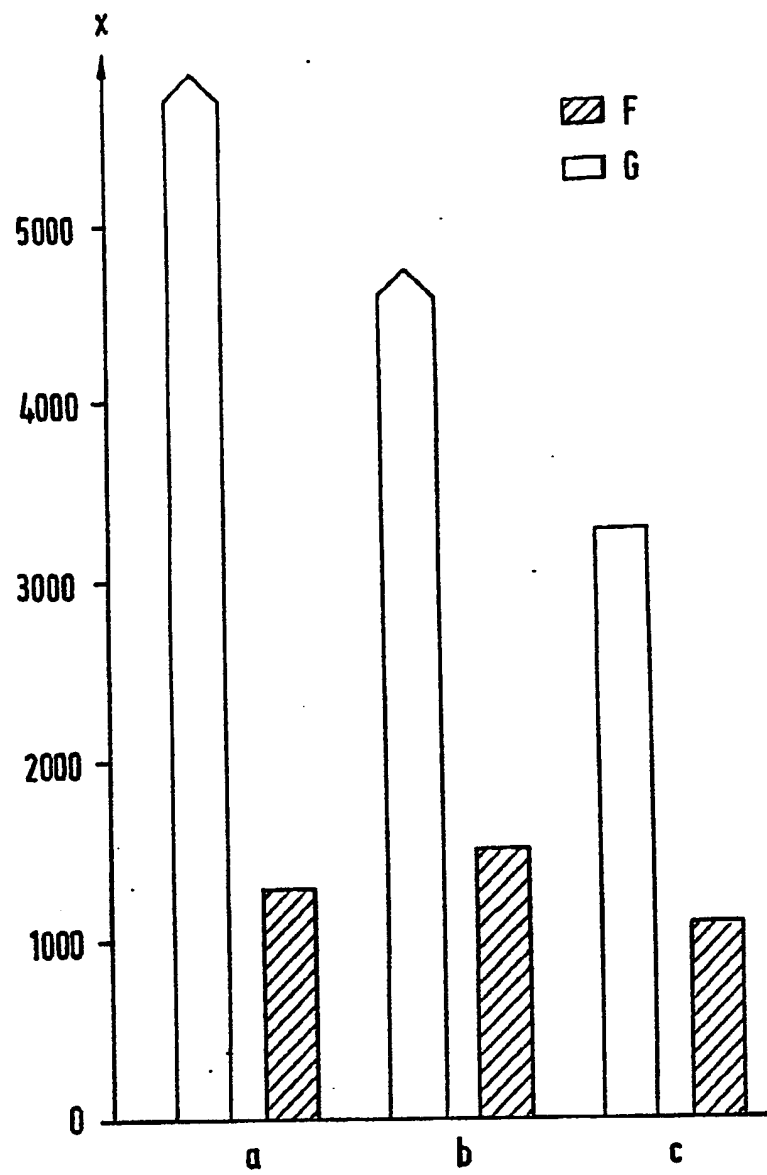


FIG. 5



"Method of treating MCrAlZ layers"

The invention relates to a method of treating MCrAlZ layers, with M from the group of metals and Z as an active element from the group of the rare earths, yttrium, hafnium, silicon or scandium, on thermally stressed engine components.

Engine components which are highly stressed thermally, such as turbine blades and jacket-ring segments, are protected from corrosion by coatings of MCrAlZ alloys and from local over-heating occurring thermocyclically by coatings of MCrAlZ alloys with an oxidic heat-insulating layer as a covering layer. In this case, M is frequently a metal or a metal alloy based on cobalt, nickel or iron.

In these coatings, the service life of the coated component is affected by the oxidation procedures on the surface of the MCrAlZ layer.

The MCrAlZ layer has a strong affinity to oxygen and

forms protective oxides on the surface of the layer. With the oxide formation the MCrAlZ layer becomes depleted in aluminium, in particular since the aluminium oxide peels off during the thermocyclic stressing and since a renewed oxide formation occurs with the consumption of aluminium, until the next peeling occurs with a reduction in the weight of the layer at the same time. As soon as the layer is so depleted in aluminium that protective aluminium oxide can no longer be formed, the rate of corrosion rapidly increases and the protective effect of the layer for the component is lost.

If the MCrAlZ layer is employed as a bonding layer between a metallic component and an oxide ceramic covering layer, it is known that although these covering layers have a heat-insulating effect, they do not constitute an obstacle to oxygen or oxidation. With oxidation stressing with thermocyclic stress reversal, the bonding layer of MCrAlZ becomes depleted in aluminium as a result of the oxide formation, and with the loosening of the aluminium oxide the entire ceramic layer peels off, which can lead to considerable secondary damage particularly in engines.

It is known from GB-A 459,848 that rare earths, including yttrium and scandium, in particular as alloying additives in nickel-chromium and

nickel-chromium-iron alloys, improve the resistance to oxidation during thermal and thermocyclic stressing. The cause of this improvement, however, is not yet fully understood. It is assumed that the de-oxidizing and de-sulphatizing effect of the alloying additives play an important part therein. It has merely been shown that alloying additives of between 0.01 and 0.5% by weight have an improving action as an active-element effect.

Meanwhile, it is customary to incorporate a Z proportion in the MCrAlZ layer as an active-element proportion of up to 6% by weight during coating. With such high proportions the peeling of aluminium oxides, which are formed on MCrAlZ layers, is effectively retarded.

The MCrAlZ layer is generally first applied in the known composition by means of low-pressure plasma injection processes for example and is then subjected to a heat treatment (homogenization). This is followed by a surface-removal machining for smoothing and setting the thickness of the layer.

This sequence of method steps has proved successful since homogenization improves the bonding of the layers and thus reduces the risk of peeling during the subsequent machining step. In addition, homogenization involves the risk of tarnishing of the layer surface.

The machining step of removal of material and smoothing is therefore performed in all known methods at the end of the treatment of MCrAlZ layers. The MCrAlZ layer must be machined in a material-removing manner so as to ensure the surface quality required in engine construction.

A disadvantage of this sequence of method steps is that despite active elements introduced during the coating the service life of the coating reaches a limit which it has not been possible to exceed until now. More precise investigations have shown that this limit is determined by the thickness of the layer, since, after the weight of the MCrAlZ layer initially increases as a result of the formation of aluminium oxide, it then drops in a substantially linear manner with the number of thermocycles by the peeling of aluminium oxide.

An object of the invention is to disclose a method as defined in the introduction, by which the disintegration of the MCrAlZ layer during thermocyclic stressing is retarded and by which the service life of the coating and thus of the protected components is improved.

The invention provides a method as claimed in claim 1.

The sequence, according to the invention, of the method steps has the advantage that an amplification of the initial increase in the weight of the coating is actually achieved during thermocyclic stressing. The thickness of protective oxide thus continues to grow, without peeling off, and the service-life limit is extended, since with an increasing number of thermocycles after achieving a maximum weight of the coating the drop in weight takes place in a substantially more reduced manner than in the case of coatings which have been treated in accordance with the conventional sequence of method steps. With hot-gas corrosion-protection layers (MCrAlZ layers) it was possible to increase the service life by more than double during thermal stressing. The service life of oxide ceramic heat-insulating layers with an MCrAlZ layer as a bonding-improving intermediate layer could be increased by a factor of 3.

This increase in the service life does not result in additional manufacturing costs, since established method steps need merely be transposed. No additional outlay is required either in planning or in apparatus in order to make use of the economic advantages of an increase in

service life.

With the sequence, according to the invention, of the method steps a higher concentration of active elements advantageously remains in the coating surface, so that the effect thereof upon oxide-formation and bonding processes on the coating surface is improved. This higher concentration by enrichment of the active elements on the coating surface results from the heat treatment.

The method according to the invention may be applied to all coatings which contain active elements, irrespectively of their composition otherwise.

In a preferred embodiment of the method, the metals M used are Fe, Co, Ni, Pt, Re, Pd, Ta, Rh or alloys thereof. In this case it is advantageous if the composition of the metals M of the coating is determined by the components contained in the part to be coated. At least an attempt is made to adapt the thermal-expansion behaviour of the coating to the thermal-expansion behaviour of the part by selecting suitable coating alloys from the above-mentioned metals M.

The active element used is preferably yttrium, which in additions of up to 1% by weight has the effect of

improving the oxidation resistance of MCrAlZ layers.

The application of MCrAlZ layers is preferably carried out by means of low-pressure plasma injection methods and the material-removing machining is performed by abrasion, for example by means of jets. This has the advantage that, in addition to the material-removal effect, a compression of the injected coating is achieved.

After the material-removal machining has taken place, the final heat treatment is preferably performed at temperatures of between 900 and 1200°C for 1 to 8 hours. At these temperatures the active elements undergo a surface-enrichment effect, the causes of which are not yet sufficiently understood, and improve the bonding of the aluminium oxide being formed on the surface.

If the MCrAlZ layer is used as a bonding layer for oxidic heat-insulating layers, the application of a heat-insulating layer preferably follows after the heat treatment has been performed. The heat-insulating layer advantageously increases the service life of the coated component during thermocyclic stressing as compared with pure hot-gas corrosion-protection layers. Because of the preferred application of this layer by means of PVD methods the heat-treated bonding layer of MCrAlZ is

produced in a gentle manner while retaining the enrichment of active elements in the surface of the MCrAlZ layer.

Zirconium dioxide with partially stabilizing additions of CaO, MgO, Y_2O_3 , Yb_2O_3 , CeO_2 or HfO_2 is preferably applied as a heat-insulating layer. It is particularly advantageous to add from 6 to 8% by weight of yttrium oxide for the partial stabilization of the tetragonal modification of zirconium dioxide.

In a preferred application of the method, components are produced thereby which have an MCrAlZ layer with an area of enrichment of active elements, preferably yttrium, close to the surface. This enrichment advantageously increases the service life during thermocyclic stressing of the component with a coating.

The enrichment preferably consists in an amplification of the concentration of at least 5 times the averaged concentration of active elements in the MCrAlZ layer. This evident amplification ensures the effectiveness of the active elements even with extreme thermal stressing of the component with a coating.

The following Examples and Figures show preferred embodiments and results of the process:

Example 1 describes the treatment method and testing of two coated components with thermocyclic stressing of a hot-gas corrosion-protection layer of MCrAlZ;

Example 2 describes the treatment of bonding layers of MCrAlZ with heat-insulating covering layers and testing the service life thereof during thermocyclic stressing;

Fig. 1 shows a testing device for the thermocyclic stressing of coated components;

Fig. 2 shows a comparison of the disintegration of hot-gas corrosion-protection layers with thermocyclic stressing;

Fig. 3 shows the micrograph of a surface of a hot-gas corrosion-protection layer of group A after 150 thermocycles at 1150°C;

Fig. 4 shows the micrograph of a surface of a hot-gas corrosion-protection layer of group B after 150 thermocycles at 1150°C, and

Fig. 5 shows increases in the service life of bonding layers of MCrAlZ with heat-insulating covering layers for three different layer systems.

Example 1

A hot-gas corrosion layer consisting of a CoNiCrAlY layer with an yttrium proportion of from 0.4 to 0.6% by weight as an active element is applied to oxidation rods of a nickel-based alloy by means of low-pressure plasma injection. After the application of the CoNiCrAlY layer the coated rods are divided into two groups A and B.

Those of group A are treated in conventional manner, by the heat treatment (homogenization) first being performed for example at 1080°C for 4 hours and then by a material-removal machining being performed for smoothing and for setting the thickness of the layer.

After the application of the MCrAlZ layer the rods of group B are first subjected to a material-removal machining for smoothing and for setting the thickness of the layer and then to a heat treatment of the smoothed coating.

Rods of groups A and B are then introduced into a testing device for thermocyclic stressing in accordance with Fig. 1 and are subjected to cyclic oxidation at maximum temperatures of 1150°C. After every 10 thermocycles the changes in weight of the individual rods are tested up to a maximum of 150 thermocycles per rod. The result is shown in Fig. 2, in which the

measurement points A represent the changes in weight of the oxidation rods of group A and the measurement points B the changes in weight of the oxidation rods of group B.

It may be clearly seen (Fig. 2) that the parts treated in accordance with the method according to the invention (group B) display a longer phase of weight increase and subsequently a weaker, reduced disintegration of the protective layer than the parts treated in accordance with the known method (group A). It is thus clear that the oxide bonding is considerably improved by the method according to the invention.

In addition, micrographs as shown in Figs. 3 and 4, which were prepared after 150 thermocycles of the coated rods, reveal considerable surface fissures, which were produced by the formation of large-volume oxide pockets, for parts of group A (Fig. 3), whereas the coating surface of the parts of group B (Fig. 4) has remained completely intact.

Example 2

Three different layer systems of an MCrAlZ layer with a covering layer of partially stabilized zirconium dioxide in the following three variations were applied to engine blades consisting of a nickel-based alloy:

Layer system a

CoNiCrAlY layer as the bonding layer
with $\text{ZrO}_2\text{-7Y}_2\text{O}_3$ as the covering layer,

Layer system b

NiCoCrAlY layer as the bonding layer
with $\text{ZrO}_2\text{-7Y}_2\text{O}_3$ as the covering layer,

Layer system c

CoNiCrAlY layer as the bonding layer
with $\text{X/ZrO}_2\text{-7Y}_2\text{O}_3$ as the covering layer.

From each variant the bonding layers were treated differently before the application of the covering layer. A group F was treated in accordance with the conventional method and a group G in accordance with the method according to the invention. The covering layers were then applied by means of PVD methods. The service life of the components was then tested with thermocyclic stressing in a device corresponding to Fig. 1 at a maximum gas temperature of 1485°C, the number of cycles until the partial peeling of the heat-insulating covering layer on the front edge of the blades constituting a comparative measure of the service life, as shown in Fig. 5.

It is clearly evident from Fig. 5 that the service life of the components of group G is more than three

times that of group F.

Fig. 1 shows a testing device for the thermocyclic stressing of coated components 1, such as engine blades 2 and 3. During the test the components 1 are alternately moved into the exhaust-gas area of a combustion chamber 4 and into the cooling-air flow of a cooling-air nozzle 5 and 6. To this end, the components 1 are secured to a slide which is displaced by a pneumatic drive 8 in the direction of arrow C. The engine blades 2 and 3 are arranged in this device in such a way that the front edges thereof are subjected to the greatest temperature changes. A maximum test temperature can be set by mixing compressed pre-heated air, which is supplied to the combustion chamber 4 in the direction of arrow D, and fuel, which is supplied to the fuel nozzle 9 in the direction of arrow E. A thermocycle comprises a heating procedure and a cooling procedure respectively.

Fig. 2 shows a comparison of the disintegration of the hot-gas corrosion-protection layers on oxide rods of groups A and B with cyclically oxidizing stressing. To this end, the change in weight is plotted in milligrams on the x-axis and the number of thermocycles on the y-axis. The weight of the two coating groups A and B initially increases after the first 10 thermocycles and then in the case of conventionally treated rods of group

A it drops in a substantially linear manner, whereas in the case of the rods of group B treated according to the invention it even rises further before a considerably reduced fall in weight occurs.

Fig. 3 shows the micrograph of a surface 11 of a hot-gas corrosion-protection layer 10 on the material 12 of an engine blade of group A after 150 thermocycles. Enlarged 500 times, the micrograph shows considerable surface fissures which are caused by the formation of large-volume oxide pockets.

Fig. 4 shows the micrograph of a surface 13 of a hot-gas corrosion-protection layer 14 on the material 12 of an engine blade of group B after 150 thermocycles. Enlarged 500 times, the micrograph shows that the coating surface 13 has remained completely intact. In addition, the average layer thickness is considerably greater than in the case of Fig. 3.

Fig. 5 shows increases in the service life of heat-insulating layers on bonding layers of MCrAlZ with heat-insulating covering layers for three different layer systems. For this purpose, the number of cycles until partial peeling of the heat-insulating covering layer on the front edge of the blades is indicated on the x-axis. For the three different layer systems a, b and c, the engine blades of group F, the bonding layer

of which has been treated in accordance with known methods, display a considerably shorter service life than the engine blades of group G which have been treated in accordance with the method according to the invention.

Claims:

1. A method of treating MCrAlZ layers as hot-gas corrosion-protection layers or as bonding layers for heat-insulation layers on thermally stressed engine components, wherein M is a metal and Z is an active element from the group of the rare earths, yttrium, hafnium, silicon or scandium, characterized in that after the application of the MCrAlZ layer a material-removing machining is first performed for smoothing and setting the thickness of the layer and after that a heat treatment of the smoothed coating is performed.
2. A method according to Claim 1, characterized in that the metals M used are Fe, Co, Ni, Pt, Re, Pd, Ta, Rh or alloys thereof.
3. A method according to one of Claims 1 or 2, characterized in that yttrium is used as the active element Z.
4. A method according to one of Claims 1 to 3, characterized in that the MCrAlZ layers are applied by means of low-pressure plasma injection methods.
5. A method according to one of Claims 1 to 4,

characterized in that the heat treatment is performed at temperatures of between 900 and 1200C for 1 to 8 hours.

6. A method according to one of Claims 2 to 5, characterized in that after homogenization a heat-insulating layer is applied.

7. A method according to one of Claims 1 to 6, characterized in that zirconium dioxide with partially stabilizing additions of CaO, MgO, Y_2O_3 , Yb_2O_3 , CeO_2 or HfO_2 is applied as a heat-insulating layer.

8. A method according to one of Claims 1 to 6, characterized in that the heat-insulating layer is applied by means of PVD methods.

9. A method substantially as herein described with reference to the accompanying drawings and either of the Examples.

10. A component with a protective layer, produced by means of methods according to one of Claims 1 to 8, characterized in that the MCrAlZ layer has an enrichment with active elements, preferably with yttrium, in the area close to the surface.

11. A component according to Claim 10, characterized in

that the enrichment consists in an amplification of the concentration of at least 5 times the averaged concentration of active elements in the MCrAl₂ layer.

12. A component substantially as herein described with reference to the accompanying drawings and either of the Examples.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

Application number
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Relevant Technical Fields

(i) UK Cl (Ed.L) C7C (FAHE, FAHL, FAHM, FAHP, FAHX, FASE, FASL, FASM, FASP, FASX, FAXE, FAXL, FAXM, FAXP, FAXX, FARE, FARP, FARL, FARM, FARX, FGA, FGZ); B3A; B3M (MN); B3D (DBR, DBAX)

(ii) Int Cl (Ed.5) C23C; B21B; B23P; B24C

Search Examiner
P G BEDDOE

Date of completion of Search
20 OCTOBER 93

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASES: WPI, CLAIMS

Documents considered relevant following a search in respect of Claims :-
1-12

Categories of documents

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&: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X	GB 2091139 A	(REFURBISHED TURBINES) see especially Claim 1; page 3 lines 10-69	1
X	GB 1261261	(UNITED AIRCRAFT) see especially page 2 lines 96-107	1-3, 8
X	GB 1210607	(INTERNATIONAL NICKEL) see especially page 2 line 114 - page 3 line 3	1
X	GB 734210	(ROLLS-ROYCE) see especially page 2 lines 16-26 and Claim 1	1
X	GB 674724	(ROLLS-ROYCE) see especially page 2 lines 83-101	1
X	EP 0074918 A2	(UNITED TECHNOLOGIES) see especially page 25 line 8 - page 27 line 4	1-4
X	US 4812107	(BBC BROWN) see especially column 3 line 57 - column 4 line 10	1

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